

Evaluation Of Commercial Ammonia Purifiers

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Summary

Point of use purification (POU) for ammonia insures consistent gas quality under changing operating conditions as required for MOCVD of GaN films in the semiconductor industry. Matheson Tri-Gas organometallic resin based purification materials (Nanochem[®] OMA) remove moisture and oxygen from an ammonia matrix below the detection limits of the instrumentation used for this study. Sub ppb level efficiencies of the organometallic resin for oxygenated impurities including sulfur dioxide and nitric oxide in inert matrix were confirmed with APIMS. The organometallic resin shows larger capacity/volume for all impurities than inorganic competitor materials, independent of the operating conditions. The lifetime of the inorganic materials significantly decreased at high flow rates or high impurity challenges. The organometallic resin therefore should guarantee high gas quality even under strongly fluctuating conditions and high impurity challenges as often found in practical usage. The purifier does not emit any metals under normal operating conditions and thus metal contamination should not be of concern.

Introduction

Point of use purification (POU) for process gases has been indispensable to semiconductor manufacturing processes. POU purifiers not only reduce impurities from gas sources such as cylinders or bulk supply units, but also prevent contaminating the gas distribution system due to cylinder changes, inadequate purge procedures or exposure to contaminated equipment. One of the fastest growing applications that require ultra pure specialty gases is MOCVD of GaN films for blue LEDs. GaN thin films are formed from trimethyl gallium and ammonia as precursors. Demands for high purity ammonia as a nitrogen source in GaN film have been increasing dramatically since GaN process tools require ammonia flow rates as high as 100 slpm.

Moisture concentrations in NH₃ gas that is withdrawn from cylinder sources from the vapor phase at high flow rates tend to increase significantly throughout the lifetime of the cylinder (1). Unsteady impurity levels can have a negative impact on the GaN film performance and complicate optimization of the film growth process. Droplet formation due to nucleate boiling at high evaporation rates, enrichment of moisture concentration at the liquid surface, and changes in the overall concentration in the residual ammonia due to preferential evaporation of ammonia are possible causes for unsteady moisture levels in the gas phase during sampling (2). Currently many customers leave close to 50% of the ammonia in the cylinder to avoid release of the residual enriched moisture in the liquid phase. POU purifiers therefore are generally recommended to ensure constant supply of high quality ammonia to the process, independent of the source gas and/or operating procedures.

Currently, commercial disposable ammonia purifiers use either Lithium chemistry based organometallic resins (Nanochem[®] OMA) or inorganic materials such as zeolite supported manganese and iron or alumina supported manganese and promise sub-ppm levels of moisture, oxygen, carbon monoxide and carbon dioxide. However, technical papers that present performance data in an ammonia matrix are scarce. Only one study showed improvements of GaN film photoluminescence after passing the ammonia used for the film growth through an inorganic based purifier (3).

This study investigates the efficiency and capacity of Nanochem[®] OMA organometallic resin for removal of moisture, oxygen and carbon dioxide. The results are compared with two commercial inorganic purifier materials. Additionally, metal emissions in ammonia matrix were measured to address concerns about possible contamination caused by the purifier and compared to competitor materials. Moisture, oxygen and carbon dioxide challenges that are consistent with the concentration range found in typical ammonia sources under standard operating conditions were used for the efficiency tests. Capacity measurements were performed at high challenges because the large capacity of all purifier materials would have required unreasonably long measurement times and large consumption of the toxic and expensive matrix gas if low challenges such as proposed by SEMI Standards (4) were used. The inorganic competitor materials were removed from the manufacturer housing and filled into identical containers to determine the intrinsic material properties and avoid artifacts caused by differences or shortcomings of the housing design.

Experimental

Purifier preparation

The materials were removed from the original purifier hardware in a purified nitrogen purged glove box and filled into three identical sample cylinders. The sample cylinders (OD: 2.54 cm, L: 38.1 cm) were equipped with 0.2 micron particle filters and diaphragm valves at the inlet and outlet. 60 ml of purifier material were filled into each bomb corresponding to a bed height of approximately 16 cm. The materials were then conditioned with ammonia for 30 – 60 min at 1 slpm to avoid exothermic temperature effects during the tests.

Gas Analysis

The efficiency of the organometallic resin for removal of oxygen, moisture, sulfur dioxide, and nitric oxide from a nitrogen matrix was measured using an Atmospheric Pressure Ionization Mass Spectrometer (APIMS). The instrument has sub-ppb level detection limits for all impurities studied.

An FTIR equipped with a liquid nitrogen cooled MCT detector and a 10 m pathlength gas cell was used for moisture measurements in ammonia matrix. The bench was modified with additional internal purge lines and enclosed in an external purge enclosure to assure low and constant background moisture levels in the beam path. Method detection limits that include uncertainties of the calibration data were less than 150 ppb.

A Gas Chromatograph equipped with a Helium Discharge Ionization Detector was used for oxygen and carbon dioxide measurements. Detection limits (LOD) based on signal-to-noise ratio (S/N=3) were estimated to be 0.1 ppm for oxygen and 0.05 ppm for carbon dioxide. The method detection limit based on regression analysis that incorporates calibration errors and variability of blanks were estimated to be 0.19 ppm for oxygen and 0.02 ppm for carbon dioxide.

Capacity and efficiency tests with oxygen was performed in ammonia matrix by mixing oxygen standards in helium matrix with purified ammonia. The test purifier inlets were typically 23 psig at 13.5 psig outlet pressure. Capacity and efficiency tests with carbon dioxide was performed in helium matrix by mixing carbon dioxide standards in helium matrix with purified helium. The performance of the purifiers for removal of carbon dioxide was only tested in helium matrix due to the reaction of carbon dioxide with the ammonia matrix. The test purifier inlets were typically 23 psig at 13.5 psig outlet pressure. Outlet concentrations of > 1 ppm were defined as breakthrough.

A porosimeter was used to determine the specific surface area of all materials studied. The tests were performed with nitrogen as adsorbent and the surface area of small pore zeolite materials ($\leq 4 \text{ \AA}$) will not be measured correctly because nitrogen will not penetrate those pores easily at liquid nitrogen temperatures used for the measurements.

Metal Emissions

After completion of the oxygen capacity tests, the exhausted sample cylinders were used for metal emission measurements. Each purifier material was tested at 3 slpm in NH_3 matrix and 50 psig using the residue method. A 0.03 μm Pall particle filter was installed at the purifier outlet similar to commercial units to trap all particulate emissions. Two empty purifier bombs were used as controls and samples were collected before and after each series of experiments to assure that the cleaning procedure was sufficient. Prior to the sample collection, each purifier was purged with NH_3 at 5 slpm and 50 psig for one hour. The ammonia flow was then decreased to 3 slpm and condensed into a liquid nitrogen cooled teflon sample vessel. The trapped ammonia was then slowly evaporated with a nitrogen stream. Actual flow rates of NH_3 during each sampling were calculated and shown in Table 1. The metal contents in the residue samples were determined by ICP-MS, ICP-OES and Flame emission spectroscopy.

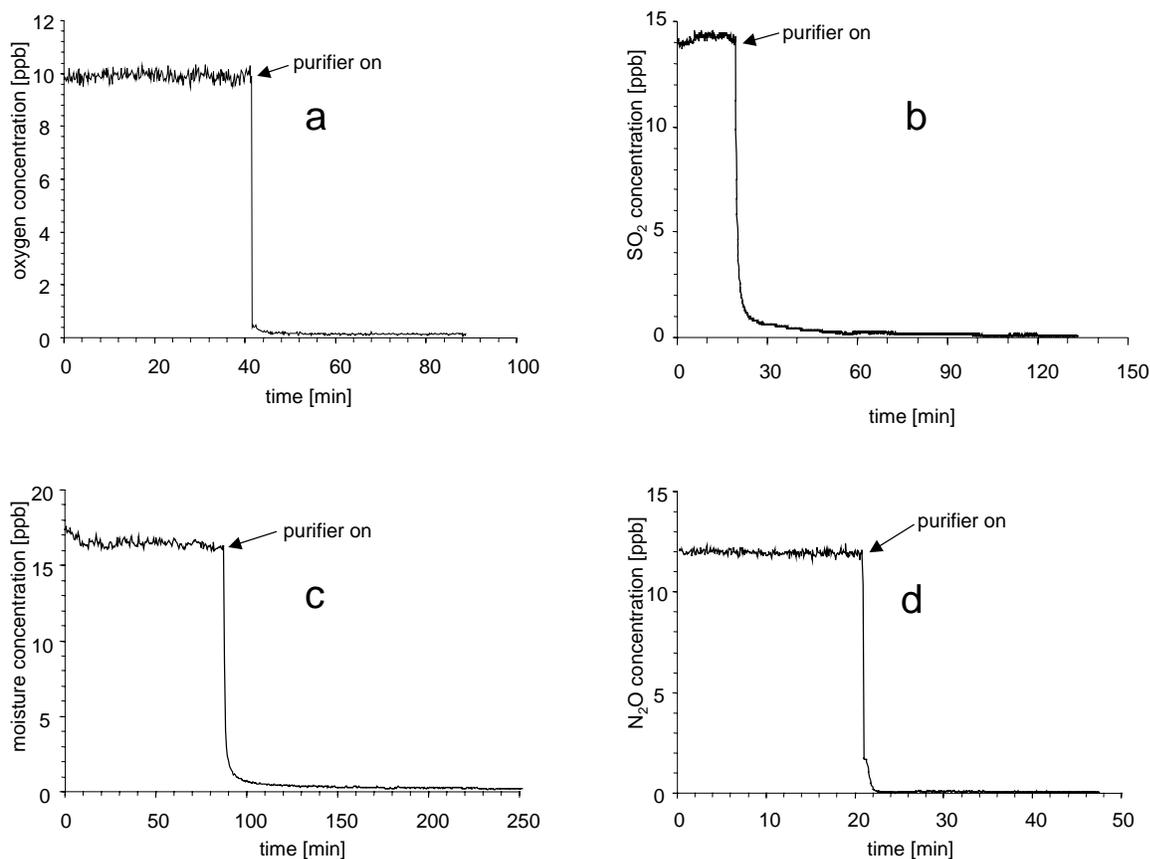
Results

Purifier Efficiency

The high efficiency of the organometallic resin for removal of moisture, oxygen, carbon dioxide, sulfur dioxide, and nitric oxide is demonstrated with APIMS in nitrogen matrix. Sub ppb levels are easily achieved as demonstrated in Figures 1a –1d. The resin used for the tests was not conditioned with ammonia. All other tests in contrast were performed with material that was exposed to ammonia similar to the commercial Nanochem[®] OMA resin that is preconditioned with ammonia and then purged with nitrogen for shipment. Since the mechanism for removal is similar both in inert gases and ammonia, it can be assumed that the efficiency for all above

impurities in ammonia matrix is also < 1 ppb. The high efficiency for moisture removal is further supported by Salim and Gupta (5), who measured sub ppb moisture backgrounds in ammonia matrix after passing through Nanochem[®] OMA resin using a highly sensitive FTIR.

Figure 1: Efficiency of organometallic resin for removal of ppb level impurities from nitrogen matrix at 2 slpm: a) oxygen; b) sulfur dioxide; c) moisture; d) nitric oxide.



Comparative efficiency tests were performed in ammonia matrix using GC and FTIR. All three purifier materials remove moisture and oxygen from ammonia at challenges of 9 to 140 ppm and flow rates between 2 and 10 slpm to levels below the detection limits of the GC and FTIR methods. Table 1 lists some of the results. The removal of carbon dioxide below the detection limit of the GC (50 ppb) was verified in He matrix and is also listed in Table 1. The detection limits in the low ppb range are significantly higher than the detection limits of the APIMS and do not represent the real efficiency of the materials but rather the limitations of the analytical instruments.

Table 1: Efficiency of organometallic resin and inorganic materials for removal of moisture, oxygen and carbon dioxide

	Impurity challenge and efficiency		
	12ppm H ₂ O 10 slpm	10ppm O ₂ 7 slpm	13 ppm *CO ₂ 10 slpm
Organometallic resin	< 150 ppb	< 100 ppb	< 50 ppb
<i>Zeolite supported manganese / iron getter</i>	< 150 ppb	< 100 ppb	< 50 ppb
<i>Alumina supported manganese</i>	< 150 ppb	< 100 ppb	< 50 ppb

* Efficiency for CO₂ was measured in He matrix.

Purifier Capacity

Figure 2a shows typical breakthrough curves of the inorganic materials and the organometallic resin for moisture measured with FTIR at a challenge of 300 – 350 ppm and flow rates of 10 slpm. Similar results were obtained with 500 ppm oxygen in ammonia matrix at 2 slpm using the GC method (Figure 2b).

Figure 2: Breakthrough curves for capacity measurements in ammonia matrix: a) moisture capacity at 10 slpm; b) oxygen capacity at 2 slpm; (A = zeolite supported manganese/iron; B = alumina supported manganese; O = organometallic resin)

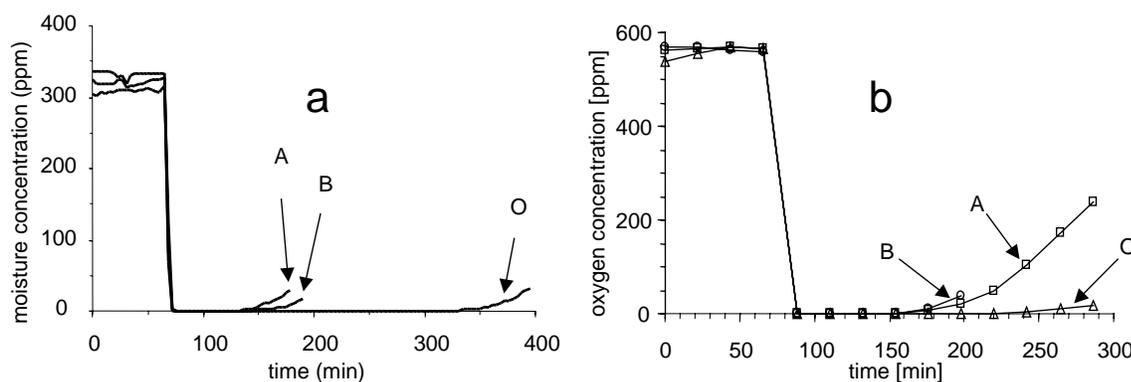


Table 2 summarizes moisture and oxygen capacities for the three materials at two different flow rates and concentrations for each impurity. The organometallic resin showed the highest capacity for both moisture and oxygen at all flow rates studied. For example the moisture capacity decreased only by about 6 % at a fivefold increase of the flow rate and 3/5 decrease in moisture concentration. The largest decrease in capacity of ~ 60% was found for the zeolite supported material whereas the capacity of the alumina/manganese purifier decreased by only 25% at the higher flow rate. Similar trends were found for the oxygen capacity with a decrease of 37% and 24% for the organometallic and alumina supported material respectively in contrast with 68% for the zeolite supported material. The capacity data measured for the zeolite supported manganese/iron material are somewhat lower than the

manufacturer data of 15 liter/liter for moisture and 5.5 liter/liter for oxygen, possibly because our tests were performed at higher challenges and flow rates than the manufacturer tests (3).

The trends in the capacity data are consistent with results of Langmuir surface area measurements using nitrogen. The materials were exposed to air prior to the measurements. The organometallic resin had the highest surface area of the three materials. The weak flow rate dependence of the organometallic resin is probably caused by very efficient packing of the spherical beads combined with fast diffusion and reaction rates of the impurities at the active sites.

Table 2: Capacity of Ammonia purifier for moisture and oxygen

Purifier material	Moisture in ammonia matrix		oxygen in ammonia matrix	
	500 ppm 2 slpm	300 ppm 10 slpm	500 ppm 2 slpm	250 ppm 7 slpm
organometallic resin	18	17	7.6	4.8
zeolite supported manganese/iron	10	4	3.8	1.2
alumina supported manganese	8	6	1.7	1.3

#Capacity value is represented by liter_(impurity)/liter_(purifier)

Metal emissions

The results of the metals emission measurements are shown in Table 3. Lithium is a major concern for the organometallic resin since the active sites of this material are based on lithium chemistry. Iron, silicon, manganese and aluminum were primary candidates for the zeolite supported purifier whereas manganese and aluminum were the main components in the alumina supported materials. No significant metal emissions were found in any sample and it can be concluded that metals emissions are not expected as long as appropriate particle filters are an integral part of the purifier hardware.

Table 3: Metal Emissions

	organometallic resin	zeolite / Mn / Fe	alumina / Mn	control 1	control 2	LOD (ppb)
Li*	<LLD	<LLD	<LLD	<LLD	0.511	0.047
Mg*	<LLD	<LLD	<LLD	1.193	<LLD	0.098
Al**	1.949	1.953	<LLD	5.371	<LLD	1.659
Si**	<LLD	2.107	<LLD	6.010	<LLD	3.763
Fe**	1.026	1.648	1.651	1.180	<LLD	0.497
Mn*	0.098	<LLD	<LLD	0.196	0.105	0.076
Cr**	0.780	1.099	1.019	0.520	0.511	0.473
Na***	1.042	<LLD	<LLD	4.157	0.321	0.075
Ca**	1.475	<LLD	1.024	12.189	0.615	0.524
K***	0.481	<LLD	<LLD	1.236	0.428	0.154

* :ICP-MS
 ** :ICP-OES
 *** :Flame Emission

Discussion and Conclusions

Large scale ammonia users such as GaN film manufacturers often might be less concerned with the performance of the purifier but worry about possible contamination of the gas stream by the purifier. The metals emission measurements clearly show that all three purifier materials are safe to use under standard operating conditions assuming that an appropriate particle filter is installed. It cannot be ruled out, however, that under extreme conditions liquefaction of ammonia in the purifier bed is possible. The ionic nature of some of the active species could cause some of the purifier material to dissolve in the liquid ammonia and possibly pass the particle filter in the liquefied state or trapped purifier particles might be washed through the filter. Condensation of ammonia in the purifier should be strongly dependent on the hardware design and therefore was not further investigated in the framework of this study.

The comparative efficiency tests in ammonia and helium matrix indicate that all three purifier materials remove moisture, oxygen, and carbon dioxide to levels below the detection limits of the analytical instruments. The strong flow rate and concentration dependency of the capacity of the zeolite supported manganese/iron and the alumina supported manganese material indicates a relatively long reaction zone compared to the bed length of the purifier. More sensitive instrumentation is expected to detect higher efficiencies of the lithium chemistry based organometallic resin (Nanochem[®] OMA) compared to the inorganic purifiers in ammonia matrix since wide reaction zones can cause low concentration breakthrough at high input challenges. The organometallic resin was additionally investigated with APIMS in nitrogen matrix and sub-ppb level efficiencies for oxygen, moisture, sulfur dioxide and nitric oxide were confirmed.

Moisture is a main contaminant in liquefied ammonia sources, and moisture levels in the gas phase are generally strongly dependent on the initial moisture levels present in the source material, operating conditions, and sampling history. Very high concentrations of moisture caused by droplet formation and concentration effects at the end of cylinder life are expected to be of less concern for the highly efficient, high-capacity organometallic resin compared to the inorganic materials that show strong flow rate and concentration dependencies. Moisture, oxygen and carbon dioxide are also present in ambient atmosphere at large concentrations and system leaks or incorrect operation procedures during cylinder change can cause intrusion of either of these impurities into the process. The performance of GaN films depends on the absence of oxygenated species and contamination has to be strictly avoided. The wealth of different sources for contamination requires a reliable safety net as provided by an appropriate point of use purifier.

Based on the results of this study, organometallic resin based Nanochem[®] OMA purifiers provide the best overall performance since capacity and efficiency are virtually independent of the operating conditions compared to the inorganic competitor materials. Efficiencies for a wide range of different impurities are high even at high flow rates and challenges. The organometallic resin also provides the largest capacity per volume which allows compact purifier hardware when space constraints are of importance.

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